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Article

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# Selecting Phthalocyanine Polymorphs Using Local Chemical Termination Variations in Copper Iodide

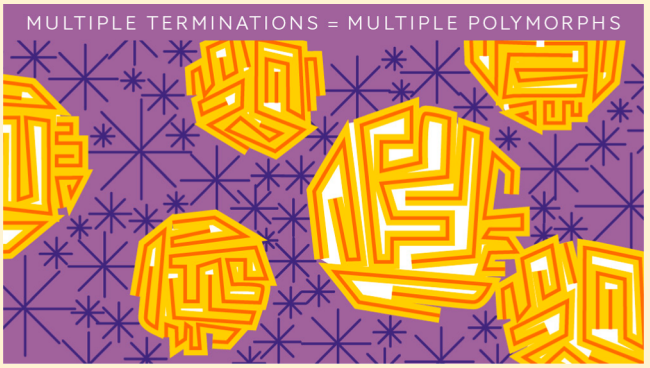
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Supporting Information

**ABSTRACT:** Copper(I) iodide (CuI) thin films are employed as a structural templating layer for the growth of metal-free phthalocyanine ($H_2Pc$) thin films. Structural polymorphs are observed in X-ray diffraction patterns when microcrystalline CuI films exhibiting copper and iodine terminated grains are used. Each polymorph is nucleated from a single termination, and distinctive crystallite morphologies are observed for each.




## INTRODUCTION

Manipulating the crystallization of organic semiconductor thin films using templating interlayers is a widespread method to produce efficient organic electronic devices.[1−4] Binary metal halides, particularly copper iodide (CuI), have been used for this purpose, and recent work has elucidated some of the fundamental aspects of this organic/inorganic interface.[5,6] The mechanism of this templating interaction is not well understood, although structural and morphological changes in the CuI layer produce concomitant changes in phthalocyanine (Pc) overlayers.[7,8] Here, we present the growth and characterization of CuI thin films on oxidized silicon ($SiO_2$) and highly ordered pyrolytic graphite (HOPG) surfaces. A combination of low energy ion scattering (LEIS) and surface potential measurements showed that both I and Cu terminated areas of the CuI surface coexist. Onto these structural templates were grown metal-free phthalocyanine ($H_2Pc$) films, and two polymorphs were observed, each localized to a single chemical termination. Understanding and controlling polymorphism in organic semiconductors can allow improvements in charge transport due to changes in the intermolecular spacings and stacking motifs.[9−11]

## EXPERIMENTAL SECTION

Thin films of CuI (30 ± 0.05 nm) and $H_2Pc$ (50 ± 0.05 nm) were grown on $SiO_2$ and HOPG substrates at a variety of substrate temperatures ($T_{sub}$), stated throughout. Bilayer films were grown without breaking vacuum to ensure cleanliness was maintained. Copper iodide (Sigma-Aldrich, UK) was used as received and evaporated from a home-built evaporator at 340 ± 0.5 °C at a rate of 0.5 ± 0.03 Å $s^{-1}$ as measured by a calibrated quartz crystal microbalance. $H_2Pc$ (Sigma-Aldrich, UK) was triply purified by thermal gradient sublimation, and the resulting crystals were used for growth from a home-built evaporator at 365 ± 0.5 °C at a rate of 0.3 ± 0.03 Å $s^{-1}$. All films were grown in a custom-built ultrahigh vacuum (UHV) chamber with a base pressure of 3 x$10^{-9}$ mbar in which organic and inorganic materials were sublimed onto substrates held at the temperatures indicated in the text. The substrate temperature was measured using a K-type thermocouple mounted close to the sample and calibrated using an optical pyrometer (IRCON).

Substrates were 10 × 10 mm pieces of thermally oxidized silicon (100) single crystal (IDB Technologies, UK) or highly ordered pyrolytic graphite (HOPG) (Agar). $SiO_2$ pieces were cleaned in isopropanol and dried in a stream of dry nitrogen, and HOPG was freshly cleaved with sticky tape before being loaded into a vacuum. Thin film XRD patterns were obtained using a PANalytical X'Pert Pro MRD diffractometer with monochromatic Cu K$\alpha_1$ radiation. Electron micrographs were recorded using field emission scanning electron microscopy (FE-SEM, Zeiss Supra 55VP) with a thin carbon coating. Atomic force microscopy (AFM) images were recorded using an Asylum research MFP-3D (Asylum Research and Oxford

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Instruments Co.) in AC mode (tapping mode) using Olympus AC240-TS silicon tips; for SKPFM AC240TM silicon tips with platinum coatings were used.

The X-ray photoemission spectroscopy (XPS) data were collected at the Warwick Photoemission Facility, University of Warwick. The samples investigated in this study were attached to electrically conductive carbon tape, mounted onto a sample bar, and loaded into a Kratos Axis Ultra DLD spectrometer, which possesses a base pressure of ~$2 \times 10^{-10}$ mbar. XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a monochromated Al $k_\alpha$ X-ray source. The measurements were conducted at room temperature and at a takeoff angle of 90° with respect to the surface parallel. The core level spectra were recorded using a pass energy of 20 eV (resolution approximately 0.4 eV) from an analysis area of 300 $\mu$m × 700 $\mu$m. The spectrometer work function and binding energy scale were calibrated using the Fermi edge and $3d_{5/2}$ peak recorded from a polycrystalline Ag sample prior to the commencement of the experiments. The data were analyzed in the CasaXPS package, using Shirley backgrounds and mixed Gaussian−Lorentzian (Voigt) line-shapes. For compositional analysis, the analyzer transmission function has been determined using Ag, Au, and Cu foils to determine the detection efficiency across the full binding energy range.

Low energy ion scattering was carried out using an IONTOF Qtac100 LEIS instrument. A 3 keV He primary ion beam was rastered over a 500 $\mu m^2$ area, with an ion beam current of 4400 nA. Total scan time was 100 s, and the ion beam dose delivered to the sample surface was $2.76 \times 10^{12}$ ions. The scattered primary ions were collected over an energy range of 500−3000 eV, to identify the scattering peaks of the Cu and I at 2379 and 2674 eV, respectively.

## RESULTS AND DISCUSSION

All thin films were grown by organic molecular beam deposition (OMBD) in ultrahigh vacuum (UHV). $SiO_2$ substrates were selected for structural studies due to the lack of low-angle diffraction peaks. Figure 1 shows the XRD patterns of the bilayer $H_2Pc$/CuI systems grown across a range of substrate temperatures. Samples grown at $T_{sub}$ = 25 ± 0.5 °C showed a single peak corresponding to diffraction from the $(41\bar{3})$ plane of $H_2Pc$; this peak is indexed using the $\beta$-phase structure of $H_2Pc$ in space group $P2_1/a$ (JCPDS no. 37-1844). This suggests structural features similar to those observed by Heutz et al. on PTCDA molecular templates.[12]

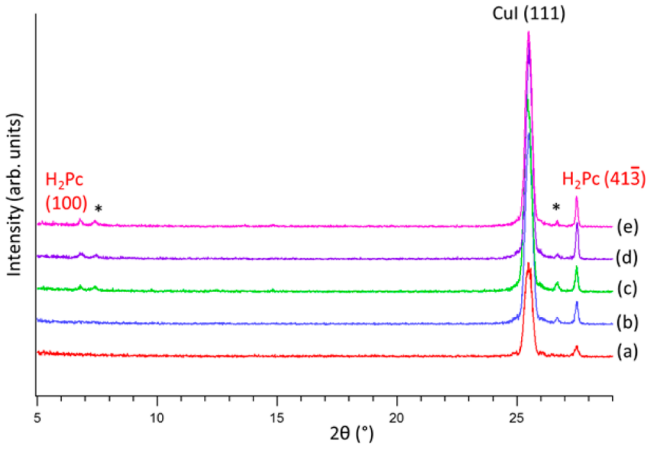



**Figure 1.** X-ray diffraction patterns of $H_2Pc$/CuI bilayers on oxidized silicon grown at the following substrate temperatures: (a) 25 ± 0.5 °C/25 ± 0.5 °C, (b) 25 ± 0.5 °C/155 ± 0.5 °C, (c) 80 ± 0.5 °C/155 ± 0.5 °C, (d) 105 ± 0.5 °C/155 ± 0.5 °C, and (e) 125 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$ 0.5 °C/CuI 0.5 °C).

Similarly to other planar Pc molecules, this suggests an orientation such that the molecular plane is parallel to the (111) oriented CuI film.[13] Large microcrystalline thin films of CuI have been previously prepared by deposition onto surfaces held at elevated substrate temperature (155 ± 0.5 °C).[5] These surfaces were prepared and, after cooling, were used for ambient substrate temperature growth of $H_2Pc$, resulting in an additional peak at 26.7° in XRD patterns. An increase in the substrate temperature during $H_2Pc$ growth to 80 ± 0.5 °C resulted in two low angle peaks (at 6.8° and 7.4°) being observed in XRD patterns in addition to the previously observed pair of high angle peaks. These peaks were also observed for higher $T_{sub}$ (see Table 1). The two low angle peaks were similar in intensity and position to those observed in polymorphic films of the comparable iron phthalocyanine (FePc) on microstructured CuI templates.[14] The presence of two peaks, only one of which can be indexed using the corresponding crystal structure (JCPDS no. 37-1844), suggested the presence of multiple polymorphs.[15] As these low angle peaks were only observed for higher substrate temperature growth, they were attributed to the out-of-plane crystallite growth observed in these cases. As single crystals could not be produced for diffraction experiments, the structure could not be solved, but if similar orientation and structural motifs are preserved, this suggests a smaller $d$-spacing (and therefore smaller intermolecular separation) in this polymorph. The high angle pair consists of the $(41\bar{3})$ peak (corresponding to lying-down molecular orientation) and another at lower angle, which cannot be indexed using the same crystal structure. This was also indicative of the growth of a separate polymorph, but both peaks were observed in $H_2Pc$ growth at ambient temperature on microcrystalline CuI. Once again, as large single crystals are not available, and assuming similar orientation and structural motifs are present, this suggests a larger $d$-spacing and therefore larger intermolecular separation. This suggests that it is the presence of large CuI grains that is responsible for the polymorphism, and polymorphs are present in both the in-plane and the out-of-plane oriented crystallites. In each case, a modification to the intermolecular separation can be inferred from diffraction data, suggesting different intermolecular spacing changes in polymorphs observed from in- and out-of-plane growth.

**Table 1. XRD Peak Positions and Assignments for $H_2Pc$/CuI Bilayers**

| $H_2Pc$ $T_{sub}$/ ±0.5 °C | CuI $T_{sub}$/ ±0.5 °C | 2$\theta$ positions and assignment |
|---|---|---|
| 25 | 25 | 27.5° $(41\bar{3})$ |
| 25 | 155 | 26.7°,[a] 27.5° $(41\bar{3})$ |
| 80 | 155 | 6.8° (100),[a]7.8°,[a]26.7°, 27.5° $(41\bar{3})$ |
| 105 | 155 | 6.8° (100),[a]7.8°,[a]26.7°, 27.5° $(41\bar{3})$ |
| 125 | 155 | 6.8° (100),[a]7.8°,[a]26.7°, 27.5° $(41\bar{3})$ |

[a]Peak positions marked with an asterisk are those that cannot be assigned Miller planes using the existing crystal structures of $H_2Pc$ available.



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Atomic force microscopy (AFM) was used to probe the morphology of these $H_2Pc$/CuI systems (Figure 2). A clear

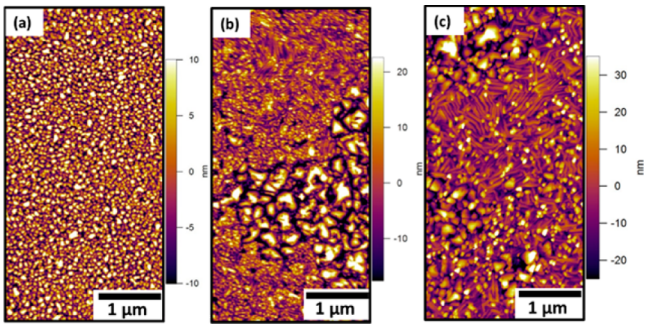



**Figure 2.** AFM topography images of $H_2Pc$/CuI bilayers on $SiO_2$ grown at $T_{sub}$ equal to (a) 25 ± 0.5 °C/25 ± 0.5 °C ($H_2Pc$/CuI), (b) 25 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$/CuI), and (c) 80 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$/CuI).

change could be observed in the morphology of the bilayers with increasing substrate temperature. The bilayers grown at $T_{sub}$ = 25 ± 0.5 °C (Figure 2a) showed films comprised of small (approximately 100 ± 10 nm) grains, typical of ambient substrate temperature templated phthalocyanines, while bilayers grown at an elevated $T_{sub}$ (Figure 2b and c) exhibit two distinct crystallite morphologies.[16] An increase in $T_{sub}$ during $H_2Pc$ growth (to 80 ± 0.5 °C) resulted in a stark difference between the crystallites with separate regions of narrow (approximately 100 ± 10 nm wide) ribbon-like crystallites coexisting with areas of block-like faceted features.

AFM imaging was not possible on samples with $H_2Pc$ growth $T_{sub}$ > 80 ± 0.5 °C due to a large increase in the roughness of these samples. Consequently, scanning electron microscopy (SEM) was carried out to analyze their morphology. The resulting images (Figure 3) demonstrated two distinct crystallite types, but also showed that the crystallites have nucleated out of the substrate plane. A further increase in the substrate growth temperature to 125 ± 0.5 °C resulted in a larger number of out-of-plane oriented crystallites, but the two previously observed crystallite morphologies could still be identified. The distinct difference in morphology suggests that

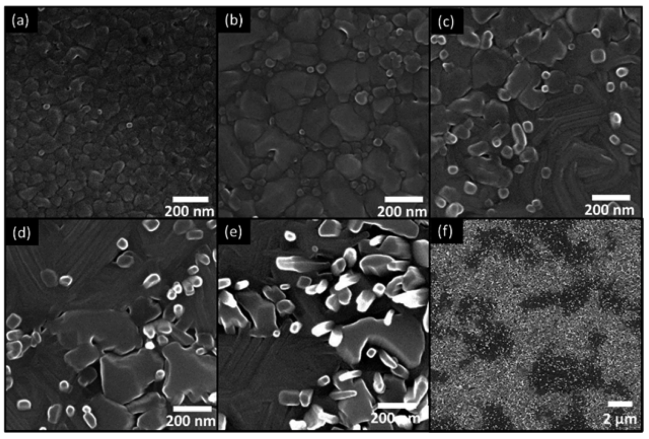



**Figure 3.** SEM images of $H_2Pc$/CuI bilayers on $SiO_2$ grown at $T_{sub}$ equal to (a) 25 ± 0.5 °C/25 ± 0.5 °C ($H_2Pc$/CuI), (b) 25 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$/CuI), (c) 80 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$/CuI), (d) 105 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$/CuI), and (e,f) 125 ± 0.5 °C/155 ± 0.5 °C ($H_2Pc$/CuI) with two different magnifications.

each crystallite type is composed of a single polymorph, and variations in the CuI layer are the underlying cause of each kind of growth.

To explore variations in the electronic structure of the surface (which may be responsible for the local differences in morphology), scanning kelvin probe force microscopy (SKPFM) was employed. As a conductive substrate was required for SKPFM, freshly cleaved HOPG was used. A lower growth temperature (80 ± 0.5 °C) was employed as this produced continuous films with CuI grain sizes comparable to those observed at 155 ± 0.5 °C on $SiO_2$. This was most likely due to increased diffusion rates of CuI adsorbates on HOPG as compared to $SiO_2$. XRD patterns (see the Supporting Information) confirmed that the CuI films on HOPG and $SiO_2$ are similarly (111) oriented. Overlaying surface potential data with simultaneously acquired topography reveal approximately 0.4 eV work function differences across the CuI (111) surface (Figure 4b). The change in work function clearly

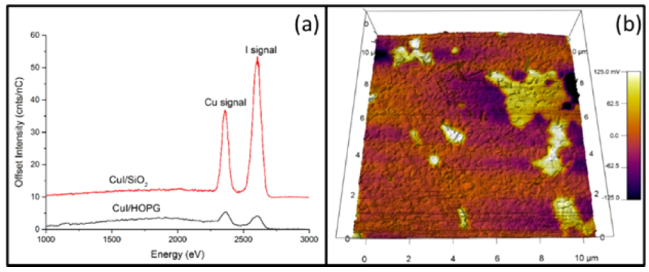



**Figure 4.** (a) LEIS data for CuI thin films on $SiO_2$ and HOPG and (b) KPFM data overlaid with topographic AFM data for CuI/HOPG ($T_{sub}$ = 80 ± 0.5 °C).

followed morphological features, which defined grain boundaries in the CuI, showing that some grains exhibited a higher work function than others. To probe the chemical identity of the topmost atomic layers of the CuI surface, low energy ion scattering (LEIS) measurements were employed (Figure 4a). Additionally, these measurements were carried out on CuI films grown at 155 ± 0.5 °C on $SiO_2$ surfaces. Iodine and copper terminations were observed in both cases, suggesting that on both substrates grains with both Cu and I terminations were present.

The combination of these measurements showed that singly terminated individual CuI grains are present and are the cause of the inhomogeneities in the electronic structure of the surface. Orthogonal projections of the structures of the two (iodine and copper) singly terminated (111) surfaces are shown in Figure S6 along with a view along the (111) plane of the CuI unit cell. This demonstrates how truncation of the CuI cell through either a copper or an iodine atom, which is situated along the (111) plane, results in a single chemical termination of the (111) surface.

Films of 50 ± 0.05 nm thick $H_2Pc$ were prepared on the CuI/HOPG layers, which showed morphological features similar to those on CuI/$SiO_2$. Careful inspection of AFM images (Figure 5) also revealed that the fiber-like morphology crystallites are all positioned such that their long axes are aligned with one of three directions, separated by 120°, with respect to the substrate within each island. An enlarged version of Figure 5c is presented in Figure S3. As the (111) surface of CuI possesses 3-fold planar symmetry, this could be the result of epitaxial growth of $H_2Pc$ crystallites, but further analysis


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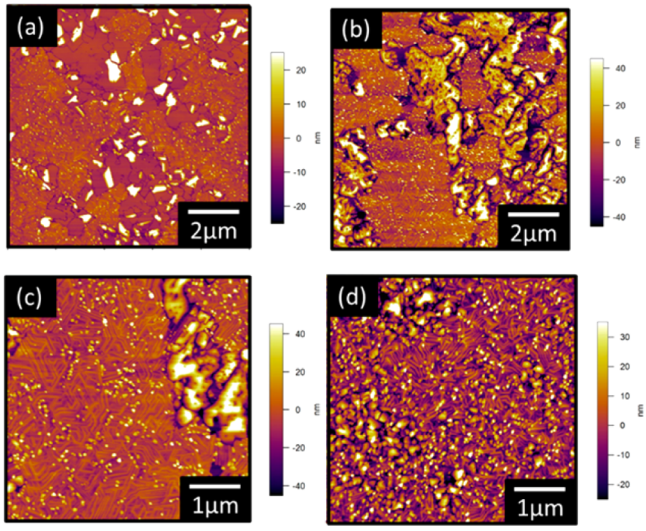



**Figure 5.** AFM topography images of (a) 10 ± 0.05 nm $H_2Pc$ and (b) 50 ± 0.05 nm $H_2Pc$ on 30 ± 0.05 nm CuI/HOPG (both layers grown at $T_{sub}$ = 80 ± 0.5 °C) with a higher magnification image of (b) seen in (c). (d) 50 ± 0.05 nm $H_2Pc$ on 30 ± 0.05 nm CuI/$SiO_2$ ($H_2Pc$ $T_{sub}$ = 80 ± 0.5 °C and CuI $T_{sub}$ = 155 ± 0.5 °C).

using model single crystal surfaces would be necessary to confirm this.[17] The block-like crystallites do not exhibit any obvious in-plane preferential orientation.

AFM images from 10 ± 0.05 nm thick films prepared using identical growth parameters showed that the growth behavior of each type of crystallite was markedly different (Figure 5). The fiber-like high aspect ratio crystals completely cover the underlying copper iodide grains, while the blockier crystals are present as discrete crystals spread over the CuI grains with bare CuI between them. The nucleation sites of the crystallites are interesting; the two different crystallite morphologies do not share underlying CuI grains, and the lateral growth of the fiber-like crystals is clearly restricted by the grain boundaries of neighboring CuI grains. The same behavior can be observed in the blockier crystallites, where the crystallite edge follows the shape of the grain boundary of the underlying CuI. These observations suggest that variations between the CuI grains are the cause of the two distinct morphologies observed.

XPS measurements were also employed to ascertain the composition of the CuI films and indicate whether significant stoichiometic variation was the reason for the large work function change (see the Supporting Information). Spectra from films grown on HOPG and $SiO_2$ showed similarly stoichiometric CuI films were produced on both surfaces (see Figures S2 and S4 and Table S1). This confirms that it is the heterogeneous crystallization on each type of CuI grain that is responsible for the observed behavior. The combination of these experimental observations showed that variations in chemical termination of CuI grains cause the profound differences in $H_2Pc$ crystallization on their surfaces.

In the case of large grained CuI films used for templated $H_2Pc$ growth, a mixture of (111) and ($\overline{1}\overline{1}\overline{1}$) surfaces was present and was terminated with either copper or iodine atoms. Each termination promoted the growth of a single polymorph of $H_2Pc$, producing a unique crystallite morphology in each case. Crystallites that nucleate and grow in-plane produced a pair of Bragg peaks at high angle (corresponding to lying-down molecular orientation), and out-of-plane crystallite growth produced a pair of peaks at low angle (corresponding to upright-standing molecules).

## CONCLUSIONS

Polymorphism was observed in $H_2Pc$ thin films grown on microcrystalline CuI (111) thin films. Two distinct morphologies were observed, suggestive of two crystallite growth habits. Surface potential and low energy ion scattering measurements revealed that local variations in workfunction caused by local differences in termination were present on the CuI thin films. Core level spectroscopy indicated that the chemical termination alone was responsible for the locally confined polymorphs. The observation of this kind of behavior allows a deeper understanding of the templating interaction. If methodology to produce singly terminated CuI films is developed, polymorphs could be selectively grown for use in organic electronic devices.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00354.

Additional XRD patterns, AFM images, and XPS spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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